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Application News

No.G310A

Gas Chromatography

Testing the Dilution Rate of Diesel in Engine Oil in Accordance with ASTM D3524

If gasoline or diesel mixes into the engine oil, it decreases the oil viscosity and prevents achievement of the proper performance as a lubricating oil. Measuring the fuel dilution rate serves as a key indicator during oil replacement, because it can determine the degradation status of the engine oil.
The test methods used to measure the fuel dilution rate are specified in standards such as U.S. ASTM D3524, D3525, and D7593. Diesel dilution rate testing methods are specified in ASTM D3524 and JPI-5S-23. This article describes an example of measuring the dilution rate of diesel in engine oil in accordance with ASTM standards.

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Preparing Samples

SAE 10W-30 engine oil was used as the diluent solvent. Six standard samples were prepared with concentrations ranging from 0.5 to 12 %. Then 0.1 g of the internal standard substance n-C_{10}*1 was added to 1 g of each standard sample. However, the samples were not diluted with CS_2.
Samples for measuring column resolution were prepared by adding 1 % n-C_{16}*3 and n-C_{18}*4, by volume, to n-C_8*2.
A standard mixture sample for deciding the end point for the diesel portion was prepared by adding 1 % n-C_{19}*5, by volume, to n-C_8.

Analytical Conditions

The analytical conditions set with reference to the various standards are indicated in Table 1.
The column resolution between n-C_{16} and n-C_{18} must be at least 3 and not more than 8 (USP).

Table 1 Analytical Conditions

Model:	Nexis™ GC-2030 AF/AOC-20i
Column:	SH-1 (5 m × 0.53 mm I.D., df = 1.00 µm), 3 pcs sets *6
Column Temp.:	70 °C (0 min) - 16 °C/min - 325 °C (0 min) Total: 15.94 min
Injection Temp.:	300 °C
Carrier Gas:	N_2, 30 mL/min
Purge Flow:	3 mL/min
Injection Method:	Split 1:5
Carrier Gas Controller:	Constant linear velocity mode
Detector:	FID
Detector Temp.:	350 °C
Injection Volume:	0.1 µL *7

*1 Tokyo Chemical Industry Co., Ltd., 99.0 % or higher
*2 FUJIFILM Wako Pure Chemical Corporation, 98.0 % or higher
*3 Tokyo Chemical Industry Co., Ltd., 98.0 % or higher
*4 Tokyo Chemical Industry Co., Ltd., 98.0 % or higher
*5 Tokyo Chemical Industry Co., Ltd., 97.0 % or higher
*6 P/N: 227-36350-01
*7 A 0.5 µL volume syringe (P/N: 000445) was used.
CS_2 was used as a rinsing solvent, instead of using samples for rinsing.
Plunger aspiration speed was slow.
Pumping was performed zero times.
The insert wool was positioned 18 mm from the top.

Chromatogram of Engine Oil Containing Diesel

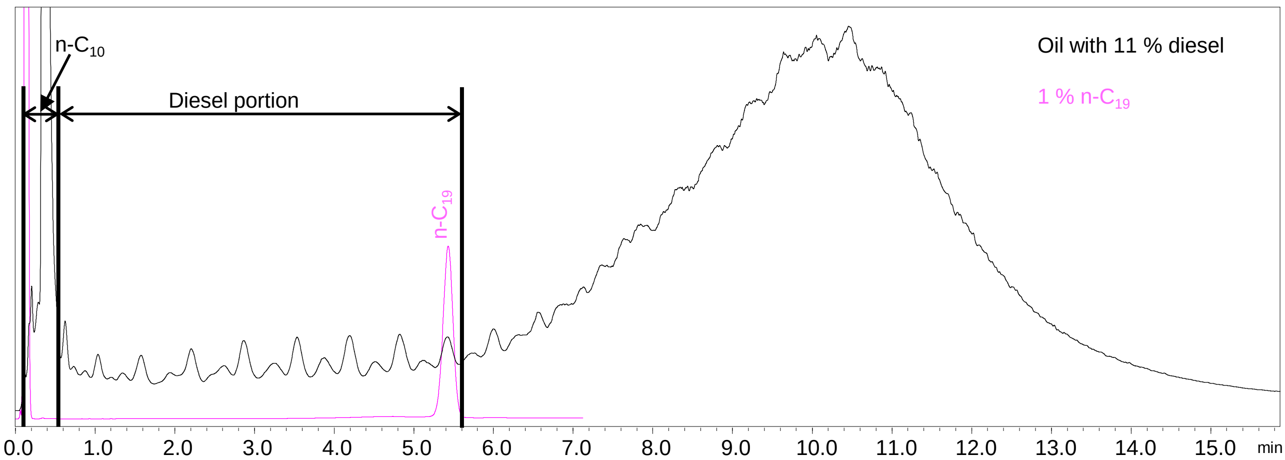

Fig. 1 Chromatogram of Engine Oil Containing Diesel

Results are shown for the diesel portion indicated in Fig. 1. To differentiate the diesel portion, samples were eluted for a retention time equivalent to n-C_{19}. The formula used to calculate the dilution rate is shown to the right.

$$C_s = C_1 + \frac{(C_2 - C_1)\ (R_S - R_1)}{(R_2 - R_1)}$$

R = Total area value for diesel / Area value for n-C_{10}

C_S: % mass of diesel dilution rate in sample
R_s: Ratio of n-C_{10} to diesel area values in the sample
R_1: Standard sample n-C_{10}-to-diesel area value ratio lower than R_s.
R_2: Standard sample n-C_{10}-to-diesel area value ratio higer than R_s.
C_1: % mass of diesel in engine oil corresponding to R_1.
C_2: % mass of diesel in engine oil corresponding to R_2.

Confirming System Performance

Results from analyzing column resolution measurement samples are shown in Fig. 2. The column resolution between n-C_{16} and n-C_{18} was 5.7. This confirmed that the system satisfies ASTM requirements for column resolution and the FID detector response factor.

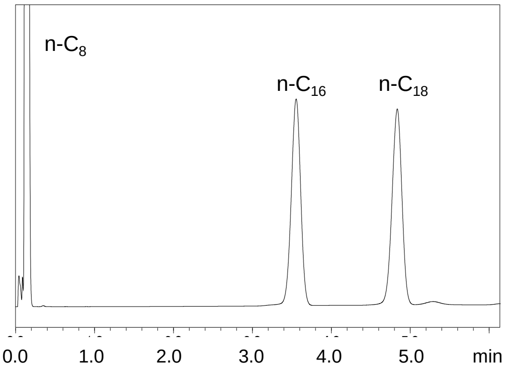

Fig. 2 Chromatogram of Column Resolution Measurement Sample

Calibration Curve

The calibration curve in Fig. 3 was prepared based on results from using the analytical conditions in Table 1 to analyze six standard samples.

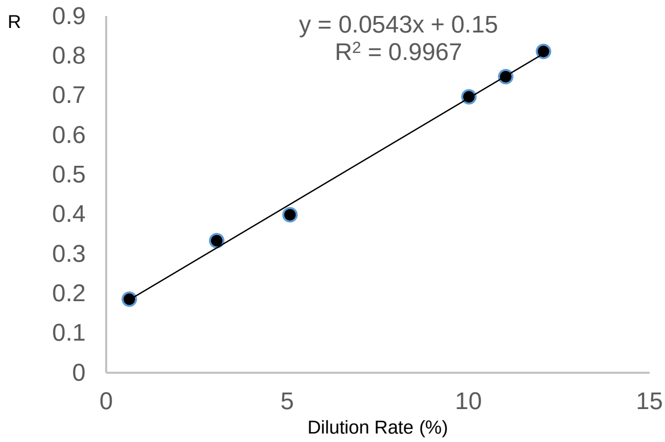

Fig. 3 Calibration Curve

Repeatability of Diesel Dilution Rates

The repeatability of diesel dilution rates is shown in Table 2. Excellent results were obtained for repeatability %RSD (n = 10). The results also confirm that within-laboratory accuracy values satisfy tolerances required by ASTM standards.

Table 2 Repeatability %RSD (n = 10) of Diesel Dilution Rates (%)

	Sample 1	Sample 2	Sample 3	Sample 4
1	3.70	4.44	10.28	10.87
2	3.80	4.35	10.43	10.68
3	3.62	4.38	10.42	10.56
4	3.85	4.34	10.30	10.93
5	3.71	4.33	10.34	11.06
6	3.75	4.36	10.57	10.87
7	3.81	4.43	10.28	11.05
8	3.84	4.38	10.28	10.71
9	3.61	4.39	10.33	10.96
10	3.70	4.35	10.41	10.68
Average	3.74	4.38	10.36	10.84
%RSD	2.29	0.84	0.90	1.58

Summary

This analysis achieved the accuracy levels required by ASTM D3524 using the indicated analytical conditions and a nitrogen carrier gas, without involving dilution with a solvent or other pretreatment steps.
Diesel dilution rate testing is governed by ASTM D7593, which describes high-throughput analysis using the backflush method. For more details, refer to Application News No. G314.
Other Application News bulletins related to fuel dilution rates are indicated in the list of references.

List of References

Standard	Item Analyzed	Application News No.
D3524	Diesel	G310
JPI-5S-23	Diesel	G311
D3525	Gasoline	G312
JPI-5S-24	Gasoline	G312
D7593	Gasoline	G313
	Diesel and biodiesel	G314

Reference Documents
ASTM D3524-14
ASTM D4626-95
JPI-5S-23-2017

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